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㉓ Ziegler type catalyst system.

㉔ A Ziegler type catalyst system for alpha-olefin type polymerization which includes R_3Y , R_2YX or a mixture thereof, at least one supported Group IVA-VIII transition metal halide and an alkyl metal compound selected from R_2YNR_2 and $R'XYNR_2$, wherein Y is Al, Ga or In. The improved catalyst system provides increased polymerization activity without significantly affecting the crystallinity of the polymer.

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1
2 The present invention relates to
3 improved Ziegler type catalyst systems for the conven-
4 tional alpha-olefin type polymerizations thereby yielding
5 polymers having a high degree of isotactic stereoregularity.

6 An object of the present invention is to provide im-
7 proved Ziegler type catalyst systems having a major increase
8 in polymerization activity while being able to control the
9 polymer crystallinity over a wide range, e.g., isotacticity,
10 wherein the catalyst system includes at least one Group
11 IVA-VIII transition metal halide, an alkyl metal cocatalyst
12 selected from the group consisting of R'_3Y or R'_2YX and mix-
13 tures thereof and an alkyl metal compound being selected
14 from R'_2YNR and $R'XYNR_2$, wherein R' is selected from the
15 group consisting of C_1 to C_{20} primary alkyl, secondary alkyl,
16 tertiary alkyl, neopentyl alkyl, branched alkyl, naphtenic,
17 or aralkyl groups, X is a halide group, R is selected from
18 the group consisting of C_3 to C_{20} bulky alkyl groups,
19 cycloalkyl groups, aryl groups, or a cyclic amine structure,
20 and Y is selected from the group consisting of aluminum,
21 gallium and indium.

22 A further object of the present invention is to provide
23 an improved process for alpha-olefin type polymerizations,
24 wherein the polymerization activity is increased without
25 adversely affecting the crystallinity of the formed polymer.

26 A still further object of the present invention is to
27 provide an improved Ziegler type catalyst system wherein
28 Catalyst poisons are consumed in situ thereby minimizing the

1 formation of atactic type polymers wherein the catalyst
2 poison $R'AlX_2$ is effectively removed from the catalyst
3 thereby making a higher number of active sites.

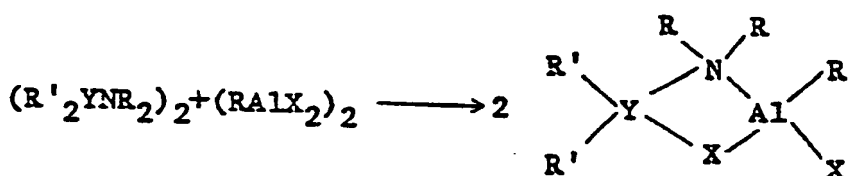
4 A still further object is the advantage over the
5 alternative catalysts of being able to use the present compounds
6 directly with any type of transition metal halide without modi-
7 fication of the commercial catalyst preparation or the polymeri-
8 zation plant.

9
10 During a Ziegler type alpha-olefin polymerization
11 which employs $TiCl_3$ in combination with R'_3Y or R'_2YX , the by-
12 product $R'YX_2$ is formed on the surface of the $TiCl_3$ thereby
13 acting as a catalyst poison (deactivator), wherein R' is selected
14 from the group consisting of C_1 to C_{20} primary alkyl, secondary
15 alkyl, tertiary alkyl, neopentyl alkyl, branched
16 alkyl, naphthenic or aralkyl groups, preferably a C_2 to C_4
17 alkyl group, X is a halide group, Y is selected from the group
18 consisting of Al , Ga or In .

19 It has been shown that the addition of small amounts
20 of $EtAlCl_2$ to a $TiCl_3$ - Et_2AlCl catalyst system dramatically
21 reduces polymerization rates (Ingberman, et. al., J. Polymer
22 Sci. A4, 2781 (1966)). Since the formation of an active cat-
23 alyst site during polymerization involves the reaction R'_2AlCl
24 $+ TiCl_3 \longrightarrow R'AlCl_2 + R'TiCl_2$ on the surface of the $TiCl_3$
25 crystal, it is apparent that the $R'AlCl_2$ catalyst poison (or
26 deactivator) is always present in such catalyst systems.

27 Likewise for the reaction of R'_3Al with excess $TiCl_3$ is:
28 $R'_3Al + TiCl_3$ (excess) $\longrightarrow R'AlCl_2 + R'_2AlCl + 3R'TiCl_2(TiCl_3)_x$

29 It has been surprisingly found that this catalyst
30 poison $R'AlX_2$ can be effectively removed from the surface of
31 the $TiCl_3$ by the addition of a compound R'_2YNR_2 or $R'XYNR_2$ to
32 the $TiCl_3$ - R'_3Al or $TiCl_3$ - R'_2AlX . The R'_2YNR_2 reacts selec-
33 tively with $R'AlX_2$ in two different ways either to remove the
34 $R'AlX_2$ by the formation of mixed dimers:



or by transalkylation to regenerate R'_2AlX and to generate $R'XYNR_2$: $R'_2YNR_2 + R'AlX_2 \longrightarrow R'XYNR_2 + R'_2AlX$. In the case of $R'XYNR_2$, the $R'AlX_2$ is simply removed by formation of a catalytically inactive mixed dimer. In either case, the $R'AlX_2$ is effectively removed from the catalyst sites, thereby resulting in a higher number of active sites per unit of catalyst volume which is reflected in a large increase in activity. When the amide (R'_2YNR_2) of the present invention is used in relatively small amounts based on the R'_3Al or R'_2AlX , the polymer isotacticity (as measured by heptane insolubles, density, tensile, etc.) is similar to or higher than that obtained with either R'_3Al or R'_2AlX alone. When higher proportions are used relative to R'_2AlX or R'_3Al , the polymer becomes less isotactic, but polymerization rates increase to even higher levels. Thus, one can achieve remarkable increases in activity from any $TiCl_3$ or $TiCl_4$ catalyst while simultaneously controlling polymer isotacticity over a wide range. Another advantage the cocatalyst supplement of the invention has over alternative catalysts is that it may be used directly with any type of $TiCl_3$ or $TiCl_4$ presently being used without modification of the commercial catalyst preparation or the polymerization plant.

The amides usable in the invention have the general structures R'_2AlNR_2 and $R'XAlNR_2$, wherein $R' = C_1$ to C_{20} hydrocarbyl group such as primary alkyl, secondary alkyl, tertiary alkyl, neopentyl alkyl, branched alkyl, cycloalkyl, or aralkyl, preferably a C_{1-12} alkyl; and $R = C_3$ to C_{20} bulky alkyl, cycloalkyl, aryl or substituted aryl groups, including ring structures such as R_2Al piperidide and Et_2Al pyrrolidide. Hindered amide groups derived from hindered secondary amines are especially preferred because they interact less strongly with the $TiCl_3$ and have greater driving

1 force to form mixed dimers with the $R'AlCl_2$ poison. Such com-
2 pounds have large, bulky R groups by virtue of branching on
3 the carbons alpha, beta or gamma to the nitrogen. Illustrative
4 examples of R groups include isopropyl, isobutyl, neopentyl,
5 3,3-diethylhexyl, 2-ethylhexyl, 2-butyl, 2-octyl, 3-pentyl,
6 cyclohexyl, cyclopentyl, 2-methyl-cyclopentyl, 3-ethylcyclohex-
7 yl, phenyl, totyl, xylyl, chlorophenyl, naphthyl and mixtures
8 including mixtures in which one R group may be a less bulky
9 saturated group such as a normal alkyl. Also, the two R
10 groups may be part of a cyclic amine structure, such as pyrrol-
11 idyl, piperidyl, and the like and their various alkyl substi-
12 tuted derivatives especially when the substituents are on the
13 carbon atoms adjacent to the nitrogen atoms, such as 2,6-diiso-
14 propylpiperidide, 2,2,6,6-tetramethylpiperidide, and the like.

15 The Y group of R'_2YNR_2 is selected from the group
16 consisting of aluminum, gallium, or indium, most preferably
17 aluminum.

18 The ratio of amide to $TiCl_3$ is between 0.05:1 to
19 5:1. The lower ratios are used together with "low aluminum"
20 containing $TiCl_3$ to make highly isotactic polymers at high
21 rates. Higher ratios are used with aluminum-containing $TiCl_3$
22 catalysts such as the commercial $TiCl_3 \cdot 0.33 AlCl_3$ catalyst.
23 "Low-aluminum" containing $TiCl_3$ refers to $TiCl_3$ catalysts
24 which have low Al because of method of formation or have had a
25 major portion of the aluminum removed as a result of subse-
26 quent reactions.

27 These new cocatalyst mixtures are useful with any
28 of the crystal modifications of TiX_3 , with solid solutions of
29 Groups II-III metal salts in TiX_3 (also referred to as "co-
30 crystallized" such as $TiCl_3 \cdot nAlCl_3$ or $TiCl_3 \cdot nMgCl_2$, and with
31 TiX_3 or TiX_4 supported on salts such as $MgCl_2$ or hydroxy-
32 chloride, oxides or other inorganic or organic supports,
33 wherein X = Cl or Br, preferably Cl. Lewis bases, alcohols,
34 carboxylic acids, etc. may also be present. The most pre-
35 ferred crystal structure is delta or pseudo delta, the latter
36 being a mixture of disordered, very small alpha and gamma

1 crystallites. This invention is also useful for increasing
2 the activity and/or stereo-specificity of supported TiCl_4 and
3 TiCl_3 -type catalysts and other supported predominantly tri-
4 valent titanium compounds. The TiCl_3 -type catalysts may be
5 prepared from TiCl_4 by any of the reduction and crystalliza-
6 tion procedures known in the art (H_2 , metal metal hydrides,
7 alkyl, etc.). Low aluminum TiCl_3 type catalysts are preferred.

8 Lewis bases can be employed in combination with the
9 trialkyl metal compound or with the Group IVA to VIII transi-
10 tion metal compound or with both components as long as they
11 do not cause excessive cleavage of metal-carbon bonds or loss
12 of active sites. A wide variety of Lewis bases may be used
13 including such types as tertiary amines, esters, phosphines,
14 phosphine oxides, phosphates (alkyl, aryl), phosphites, hexa-
15 alkyl phosphoric triamides, dimethyl sulfoxide, dimethyl for-
16 mamide, secondary amines, ethers, epoxides, ketones, saturated
17 and unsaturated heterocycles, or cyclic ethers and mixtures
18 thereof. Typical but non-limiting examples are diethyl ether,
19 dibutyl ether, tetrahydrofuran, ethylacetate, methyl p-toluate,
20 ethyl p-anisate, ethyl benzoate, phenyl acetate, amyl acetate,
21 methyl octanoate, acetophenone, benzophenone, triethylamine,
22 tributyl amine, dimethyldecylamine, pyridine, N-methylpiperi-
23 dine, 2,2,6,6-tetramethylpiperidine, and the like. Especially
24 useful in combination with the trialkyl metal cocatalyst are
25 Lewis bases whose complexing ability toward the cocatalyst is
26 "hindered" sufficiently by steric and/or electronic effects to
27 cause appreciable dissociation of the trialkyl metal-Lewis
28 base complex under polymerization conditions. Although a wide
29 range of mole ratios may be used, dissociation of the complex
30 as measured on a 1:1 complex is normally in the range of 1-99
31 mole %, more preferably 5-95%, and most preferably greater
32 than 10% and less than 90%. Steric hindrance is achieved
33 by bulky substituents around the heteroatom which reduces
34 the accessibility of the base functionality to the Lewis
35 acid, that is, the trialkyl metal compound. Electronic
36 hindering is obtained by placing electron withdrawing sub-

stituents on the heteroatom to reduce the electron density on basic heteroatom. Aromatic substituents are especially useful because they are relatively unreactive toward other catalyst components. Hindered Lewis bases derived from piperidines, pyrrolidines, ketones, tetrahydrofurans, secondary and tertiary aromatic amines and tertiary aliphatic amines are preferred, with the hindered nitrogen bases being most preferred. Non-limiting examples of sterically hindered bases include 2,2,6,6-tetramethylpiperidine, 2,2,5,5,-tetramethylpyrrolidine, 2,2,5,5,-tetramethyltetrahydrofuran, di-tert-butylketone, 2,6-diisopropylpiperidine, ortho-tolyl t-butyl ketone, methyl 2,6-di-tert-butylphenylketone, diisopropylethylamine, t-butyl dimethylamine, 6-methyl-2-isopropylpyridine, and the like. Electronically hindered Lewis bases include diphenylamine, di-ortho-tolylamine, N,N-diethyl-aniline, di-ortho-tolylketone, and the like. Since aromatic substituents are also bulky, some of the electronically hindered bases can also have a steric contribution to the hindrance. Especially preferred hindered amines are 2,2,6,6-tetramethylpiperidine, 2,2,5,5,-tetramethylpyrrolidine and the diarylamines. Completely hindered bases, such as 2,6-di-tertiarybutylpyridine, and the like, which complex the alkyl metal cocatalyst too weakly, are ineffective for improving stereospecificity and are excluded from this invention.

Further increases in activity or stereospecificity may be obtained by premixing the transition metal component with either the amide or the alkyl metal, or both.

The amide effect is obtained with all the usual polymerization conditions. Thus solvent, temperature and monomer concentrations are not critical. Increased activity is obtained with all alpha olefins from ethylene to C₁₀ and higher as well as in copolymerizations such as ethylene/ α -olefin, ethylene/diolefin, propylene/ α -olefin, propylene/diolefin and ethylene/ α -olefin/diene copolymerizations. The amount of alkyl metal cocatalyst is usually in the range of 0.1:1 to 20:1, preferably 0.5:1 to 10:1 mole ratio of

1 alkyl metal to transition metal compound. It is feasible
2 using the hindered amides and hindered Lewis bases to employ
3 higher mole ratios, up to 200:1 or higher, to achieve higher
4 activity at high stereospecificity. The most preferred mole
5 ratios with the hindered components is in the range 5:1 to
6 200:1 alkyl metal plus amide to transition metal compound.

7 The concept of the invention can be restated as
8 follows. Two types of alkyl metal compounds have been found
9 to be effective for greatly increasing the activity of Ziegler
10 catalysts, especially for propylene polymerization. These are
11 alkyl aluminum dialkylamides and alkyl chloroaluminum dialkyl
12 amides. The amides most preferably are sterically hindered.
13 Both types are believed to operate by selectively scavenging
14 the $R'AlCl_2$ poison from the catalyst through the formation of
15 mixed dimers. The dialkylaluminum additives are preferred
16 because they regenerate the desirable R_2AlCl by reaction with
17 $RAlCl_2$. However, the corresponding alkyl chloroaluminum amides
18 are also effective additives for simply scavenging $RAlCl_2$.

19 These latter have the advantage over the dialkylaluminum types
20 in that they have little, if any, polymerization activity so
21 that the amounts used need not be so carefully controlled.

22 When the dialkylaluminum amide additives are used
23 in excess over the amount of $R'AlCl_2$ produced by the catalyst
24 reactions, they are capable of forming active sites which
25 yield lower isotacticity polymer. Therefore, these additives
26 are preferably used in 5 to 50 mole % based on $TiCl_3$
27 in the absence of extrinsic sources of $R'AlCl_2$. 50-100
28 mole % should be used when added $R'AlCl_2$ plus that formed by
29 reacting R'_2AlCl with $AlCl_3$ in the titanium component is in
30 the overall polymerization system. The best results are
31 obtained when the molar amount of additive is approximately
32 equal to the molar amount of $R'AlCl_2$ produced before and
33 during polymerization.

34 The alkyl groups on the aluminum compound containing
35 2 to 12 carbons per alkyl group all produce higher
36 activity catalysts. However, for propylene and higher alpha

1 olefins, polymer isotacticity decreases with increasing alkyl
2 chain length. Therefore, C₂ to C₄ alkyl groups are preferred
3 when isotactic polymers are desired.

4 The halide group in the aluminum components of the
5 catalyst is preferably chloride or bromide, with chloride
6 being most preferred.

7 The alkyl groups attached to the amide nitrogen are
8 preferably attached to secondary or tertiary carbons to
9 achieve sufficient steric hindrance. Primary alkyls are use-
10 ful only when there is sufficient branching on the carbon atom
11 beta or gamma to the nitrogen. Open chain as well as cyclic
12 groups may be used. The most preferred groups are isopropyl,
13 t-butyl and cyclohexyl groups.

14 The additives appear to be useful with any Group
15 IVA-VIII Ziegler transition metal catalyst which produces
16 R'AlCl₂ poison by reaction with aluminum alkyls. Trivalent
17 titanium and vanadium chlorides are preferred with those
18 having low aluminum content being most preferred. The addi-
19 tives also appear to be generally useful for any monomer and
20 mixtures of monomers.

21 When the dialkylaluminum amide additives are used
22 in combination with aluminum trialkyl compounds, the preferred
23 transition metal component is supported TiCl₃ or TiCl₄ on
24 salts such as MgCl₂ or hydroxychloride in which at least one
25 Lewis base is also present. An excess of amide over the
26 aluminum trialkyl may be used with supported TiCl₄ catalysts
27 to further increase isotacticity. Thus the mole ratio
28 of aluminum trialkyl to amide may be 1 to 50 to
29 50 to 1, preferably 1 to 10 to 10 to 1. The molar
30 ratio of the trialkyl metal compound to the supported transition
31 metal compound is 0.5 to 1 to 200 to 1 or higher,
32 more preferably 5 to 1 to 100 to 1. Lewis bases
33 are normally added in less than stoichiometric amounts based
34 on the trialkyl metal cocatalyst or the nitrogen-containing
35 metal alkyl compound, preferably 0.1 to 1 to 1 to
36 1. However, the hindered Lewis bases may be added in greater

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1 than equimolar amounts, from 0.1 to 1 up to 10:1
2 mole ratio, to obtain higher stereospecificity without a major
3 loss of activity which would occur with unhindered bases.

4
5 The advantages of the catalyst
6 system, the process for the alpha-olefin polymerization and
7 the compositions of the mixed dimers of the
8 present invention can be more readily appreciated by
9 reference to the following Examples and tables.

10 EXAMPLE 1

11 A series (A-G) of polymerization runs was carried
12 out in a 1 liter baffled resin flask fitted with an efficient
13 reflux condenser and a high speed stirrer. In a standard
14 procedure for propylene polymerizations, 475 ml n-heptane
15 (< 1 ppm water) containing 10 mmole Et_2AlCl (1.20 g) was
16 charged to the reactor under dry N_2 heated to reaction tem-
17 perature (65°C) and saturated with pure propylene at 765 mm
18 pressure. The TiCl_3 (1.00 g) (6.5 mmole) was charged to a
19 catalyst tube containing a stopcock and a rubber septum cap.
20 Polymerization started when the TiCl_3 was rinsed into the
21 reactor with 25 ml n-heptane from a syringe. Propylene feed
22 rate was adjusted to maintain an exit gas rate of 200-500
23 cc/min at a pressure of 765 mm. After one hour at tempera-
24 ture and pressure, the reactor slurry was poured into one
25 liter isopropyl alcohol, stirred 2-4 hours, filtered, washed
26 with alcohol and vacuum dried.

27 The TiCl_3 was prepared by reduction of TiCl_4 with
28 Et_2AlCl followed by treatment with diisopentyl ether and
29 TiCl_4 under controlled conditions, yielding a high surface
30 area delta TiCl_3 having low aluminum content (hereinafter
31 "low aluminum" TiCl_3).

32 In Runs B-E, the diethyl aluminum diisopropylamide
33 ($\text{Et}_2\text{AlN}(\text{iPr})_2$) was added to the reactor together with the
34 Et_2AlCl . The results summarized in Table I following show
35 that activity increased sharply up to 1 mmole amide, then
36 more slowly up to 3 mmoles amide. The percent heptane in-

1 solubles (also called isotacticity index) remained essen-
2 tially constant, then decreased slightly at 3 mmoles amide.

3 Runs F and G show that still larger increases in
4 activity are obtained by premixing the $TiCl_3$ with either the
5 amide or the Et_2AlCl .

6 Thus, the addition of only 5-30 mole % amide based
7 on Et_2AlCl , or about 7-50 mole % based on $TiCl_3$, resulted in
8 25-250 percent increase in polymerization rate over Control
9 Run A.

10 The increased activity was not due simply to higher
11 dialkyl aluminum concentration because 13 mmoles Et_2AlCl gave
12 only 34.1 activity.

13 TABLE I

14 PROPYLENE POLYMERIZATION
15 $Et_2AlN(iPr)_2$ Additive

16	Run	$Et_2AlN(iPr)_2$ Mmoles	Rate g/g $TiCl_3$ /hr	% Heptane Insolubles(a)
17	A(Control)	0	34.2	95.7
18	B	0.5	48.2	94.7
19	C	1	52.2	93.3
20	D	2	51.8	94.9
21	E	3	54.2	92.0
22	F	2(b)	65.2	94.6
23	G	3(c)	83.2	91.7
24	(a) Insoluble in boiling n-heptane based on total 25 product, including alcohol-solubles minus catalyst.			
26	(b) Mixed $TiCl_3$ + amide in 12 ml n-heptane, 50°C. 15 27 min. before charging to reactor containing the 28 Et_2AlCl .			
29	(c) Mixed $TiCl_3$ + Et_2AlCl in 10 ml n-heptane, 25°C. 30 30 min. before charging to reactor containing the 31 $Et_2AlN(iPr)_2$.			
32				

33 The results as shown by the above data are that the
34 technique of the invention can be used to more than double
35 activity without a significant decrease in the heptane solu-
36 bles of the resulting polymer.

37 EXAMPLE II

38 The procedure of Example I was repeated for addi-
39 tional Runs H-N except that diethyl aluminum dicyclohexyl-

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amide ($\text{Et}_2\text{AlN}(\text{cyC}_6)_2$) was used instead of the diisopropylamide. Commercial delta cocrystallized $\text{TiCl}_3 \cdot 0.33 \text{ AlCl}_3$ (Stauffer AA grade) (1.00 g) (5 mmoles) was used instead of TiCl_3 . (This commercial TiCl_3 catalyst has lower activity than the "low-aluminum TiCl_3 catalyst" used in Example I). By "cocrystallized" it is meant that the AlCl_3 is an integral part of the crystal lattice of the TiCl_3 . The results are summarized as follows in Table II.

TABLE II
PROPYLENE POLYMERIZATION
 $\text{Et}_2\text{AlN}(\text{cyC}_6)_2$ Additive

Run	$\text{Et}_2\text{AlN}(\text{cyC}_6)_2$ Mmoles	Rate g/g TiCl_3 AA/hr	% Heptane Insolubles(a)
H(Control)	0	20.9	93.7
I	0.30	23.7	94.0
J	0.625	28.5	93.8
K	2	36.8	89.9
L	3	40.0	84.7
M	2(b)	32.3	93.0
N	2(c)	30.9	94.0
(a)	Same as (a) in Table I.		
(b)	Premixed $\text{TiCl}_3 \cdot 0.33 \text{ AlCl}_3$ + amide in 10 ml n-heptane, 25°C, 30 min. before charging to reactor containing the Et_2AlCl .		
(c)	Premixed $\text{TiCl}_3 \cdot 0.33 \text{ AlCl}_3$ + Et_2AlCl in 5 ml n-heptane, 25°C, 30 min. before charging to reactor containing the $\text{Et}_2\text{AlN}(\text{cyC}_6)_2$.		

The results in Table II show that activity nearly doubled upon addition of 3 mmoles amide (60 mole % on TiCl_3). In contrast to the results in Example I using an essentially aluminum-free TiCl_3 , the polypropylene isotacticity decreased substantially with increasing amounts of amide, but at least a 40% increase of activity could be obtained without loss of isotacticity.

Runs M and N show that premixing either the amide or the Et_2AlCl with $\text{TiCl}_3 \cdot 0.33 \text{ AlCl}_3$ resulted in a smaller activity increase than was obtained without premixing (Run K), but the heptane insolubles were raised back up to the Control

1 (Run H). Thus, with premixing an approximately 60% increase
2 in activity could be obtained without loss of isotacticity.

3 EXAMPLE III

4 The procedure of Example II, Run K, was repeated
5 except that 2 mmoles diethyl aluminum diethylamide was added
6 instead of dicyclohexylamide. Polymerization rate was 24.9
7 g/g $\text{TiCl}_3 \cdot 0.33 \text{ AlCl}_3$ /hr and heptane insolubles was 94.1 per-
8 cent. Therefore, the unhindered diethylamide was much less
9 effective than the hindered dicyclohexylamide in increasing
10 catalyst activity.

11 EXAMPLE IV

12 The procedure of Example I, Runs B and D, was re-
13 peated using diethyl aluminum dicyclohexylamide with similar
14 results (40.3 and 47.6 g/g TiCl_3 /hr vs 34.2 for the Control).

15 EXAMPLE V

16 The procedure of Example I, Run E was followed ex-
17 cept that brown TiCl_3 (most beta) was used (prepared by mixing
18 $\text{Et}_2\text{AlCl} + \text{TiCl}_4$ in n-hexane at -30°C and heating to 65°C for
19 1 hr, filtered, washed with n-hexane and vacuum dried). Poly-
20 merization rate increased to 41.4 g/g TiCl /hr from 18.0 for
21 the Control run performed in the absence of $\text{Et}_2\text{AlN}(\text{iPr})_2$.

22 EXAMPLE VI

23 A titanium catalyst supported on MgCl_2 was prepared
24 by ball milling 20 g anhydrous MgCl_2 , six ml ethylbenzoate and
25 3 ml methylpolysiloxane for 100 hr at room temperature. The
26 solid was treated with an equimolar amount (based on MgCl_2) of
27 1 M AlEt_3 at 100°C for 1.5 hours, filtered and washed with
28 heptane. This product was treated with excess 40% TiCl_4 in
29 heptane at 65°C , 2 hours, then with 90% TiCl_4 , 65°C , 1.5 hours,
30 washed thoroughly with heptane and vacuum dried, yielding a
31 brown powder containing both TiCl_3 and TiCl_4 . The procedure
32 of Example I, Runs A (Control) and D were followed except that
33 1 g of the supported catalyst was used in place of TiCl_3 .
34 Polymerization rate in the presence of amides increased to
35 75.7 from 21.1 in the Et_2AlCl Control. Heptane insolubles
36 increased to 46.4 from 35.8.

1 EXAMPLE VII

2 Polymerization runs were made in a stirred auto-
3 clave at 100 psi propylene pressure plus hydrogen for mol-
4 ecular weight control using pentane diluent, 60°C, 2 hours.
5 The Control run using 10 mmoles Et_2AlCl /5 mmoles $\text{TiCl}_3 \cdot 0.33$
6 AlCl_3 (Stauffer AA grade) produced 495 g polypropylene/g
7 TiCl_3 . Repeating the same run but also adding 2.5 mmoles
8 $\text{Et}_2\text{AlN}(\text{iPr})_2$ increased catalyst efficiency to 612 g/g TiCl_3 .

9 EXAMPLE VIII

10 Ethylene was polymerized following the procedure
11 of Example I, Run A. During the first 25 minutes, the ethyl-
12 ene absorption rate decreased from 370 cc/min to 330 cc/min.
13 At this point, 3 mmoles $\text{Et}_2\text{AlN}(\text{iPr})_2$ in 10 ml n-heptane was
14 added. The ethylene absorption rate gradually increased to
15 360 cc/min during the next 35 minutes. Thus, the rate of
16 ethylene polymerization is also increased by the addition of
17 a dialkylaluminum amide, but the effect is much smaller than
18 for propylene polymerization.

19 EXAMPLE IX

20 An ethylene-propylene copolymerization was carried
21 out in a similar manner to the procedure of Example VIII
22 except that only 0.5 g TiCl_3 plus 5 mmoles Et_2AlCl was used.
23 The monomer feed rates were set at 150 cc/min ethylene and
24 1350 cc/min propylene. During the first 20 minutes, the
25 absorption rate was 550 cc/min. At this point, 1.5 mmoles
26 $\text{Et}_2\text{AlN}(\text{iPr})_2$ in 10 ml n-heptane was added and the absorption
27 rate increased to 750 cc/min for the next 15 min.

28 EXAMPLE X

29 The procedure of Example I was followed for a series
30 of Runs T'-X' and AA except that halogenated aluminum amides
31 were used together with various alkyl aluminum compounds. The
32 preparation of low aluminum TiCl_3 prepared by the technique
33 described in Example I was used. The results are summarized
34 as follows in Table IV.

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TABLE IV				
	Run	Mmoles RnAlX ₃ -n	Mmoles RXAlN(iPr) ₂	Relative Activity
1				
2				
3				
4	Control	10 Et ₂ AlCl	--	100
5	T'	--	5 EtClAlN(iPr) ₂	8.2
6	U'	5 EtAlCl ₂	5 EtClAlN(iPr) ₂	8.7
7	V'	5 Et ₂ AlCl	5 EtClAlN(iPr) ₂	155
8	W'	5 Et(C ₁₂)AlCl	5 EtClAlN(iPr) ₂	180
9	X'	5 (C ₁₂) ₂ AlCl	5 EtClAlN(iPr) ₂	86
10	AA	5 AlEt ₃	5 EtClAlN(iPr) ₂	576
11	BB	10 Et ₂ AlCl	2 EtClAlN(iPr) ₂	157
				% Heptane Insoluble
				95.6
				--
				--
				94.0
				83.2
				54.2
				62.0
				93.9

The data from these experiments show the following:

(1) Aluminum amides containing less than two alkyl groups are inactive alone (Run T) or when mixed with RAlCl_2 (Run U), because no R_2AlCl is present for active site formation.

(2) Alkyl chloroaluminum amides increase the activity of catalysts containing R_2AlCl (Runs V', W' and BB).

(3) Long chain alkyl groups in the R_2AlCl component decrease heptane insolubles (Runs W' and X').

(4) AlEt_3 yields very high activity in the presence of the amide (Run AA) but heptane insolubles are substantially less than in the Et_2AlCl control.

(5) Increasing the ratio of Et_2AlCl : amide from 5:5 (Run V) to 10:2 (Run BB) gave no additional improvement in activity or heptane insolubles.

EXAMPLE XI

The procedure of Example I, Run B, was followed except that aluminum triethyl was used in combination with the diethyl aluminum diisopropylamide and the transition metal catalyst (0.2 g) was TiCl_4 supported on MgCl_2 . The catalyst was made by ball milling 5 moles MgCl_2 with 1 mole ethylbenzoate for one day, adding 1 mole TiCl_4 and milling 3 days, then treating with neat TiCl_4 at 80°C , 2 hours, washing with heptane and vacuum drying. The catalyst contained 3.44% Ti.

TABLE V

Run	Mmoles AlEt_3	Mmoles $\text{Et}_2\text{AlNiPr}_2$	Rate g/g Cat/hr	% Heptane Insolubles
Control	1	0	244	83.1
A	1	0.2	268	83.8
B	1	1	299	87.3
C	0	1	0	--
D	0.25	1	20	96.8
E	1	3	267	90.4

The amide additive increased both activity and heptane insolubles with increasing concentrations (Runs A, B and E vs. control) although the amide was inactive alone (Run C). Keeping the amide concentration constant and decreasing the

1 AlEt_3 concentration (4 amide/1 AlEt_3) reduced activity but gave
2 very high heptane insolubles (Run D vs. Run B).

3 EXAMPLE XII

4 The procedure of Example XI was followed except that
5 $\text{t-Bu}_2\text{AlEt}$ was used instead of AlEt_3 .

6 TABLE VI

7 Run	8 Mmoles t-Bu ₂ AlEt	9 Mmoles Et ₂ AlNiPr ₂	10 Rate g/g Cat/hr	11 % Heptane Insolubles
9 Control	1	0	248	93.8
10 F	1	1	265	93.8
11 G	1	1.2	245	94.4
12 H	1	1.5	258	94.5

13 An excess of amide over the aluminum trialkyl increased both
14 activity and heptane insolubles over the control run.

15 EXAMPLE XIII

16 The procedure of Example XI, Runs B and E, was
17 followed except that $\text{Et}_2\text{AlNEt}_2$ was used in place of $\text{Et}_2\text{AlNiPr}_2$.
18 Polymerization rates were 230 and 246, respectively, no improve-
19 ment over the control rate of 244. Heptane insolubles were
20 84.5 and 84.9, essentially unchanged from the control 83.1%.
21 Comparison of these runs with Example IX, Runs B and E, show
22 that small, non-hindered alkyl groups attached to the amide
23 nitrogen are not effective whereas bulky groups, such as iso-
24 propyl, increase both activity and stereospecificity.

25 EXAMPLE XIV

26 A new preparation of supported catalyst was used
27 which contained 3.16% Ti.

28 TABLE VII

29 Run	30 Mmoles AlEt ₃	31 Mmoles Et ₂ AlNiPr ₂	32 Mmoles EB	33 Rate	34 % HI
31 Control	1	0	0	506	81.6
32 I	1	1	0	468	85.4
33 J	1	1	0.1	249	93.9
34 K	1	1	0.2	140	97.0
35 L	1	1.2	0.2	166	96.4
36 M	1	3	0.2	282	92.2

These experiments show that small amounts of a Lewis base added to the cocatalyst system result in a major improvement in the stereospecificity while still retaining good activity.

EXAMPLE XV

The procedure of Example XIV was followed except that hindered amides and a highly hindered Lewis base were used.

TABLE VIII

Run	Mmoles AlEt ₃ -	Mmoles Amide	Mmoles Amine (3)	Rate	% HI
N	0.5	1.5 A (1)	0.5	169	98.1
O	0.88	3.12 B (2)	0.88	343	98.4
P	0.64	1.36 B (2)	0.14	387	95.8

(1) A = Et₂AlN(cyC₆H₁₁)₂

(2) B = Et₂Al-2,2,6,6-tetramethylpiperidide

(3) Amine = 2,2,6,6-tetramethylpiperidine.

Comparison with the results in Table VII shows that the combination of hindered amide and hindered amine increased both activity and stereospecificity to higher levels than were achieved with the unhindered amides and bases.

EXAMPLE XVI

The procedure of Example XV was followed except that an unhindered Lewis base (ethylbenzoate = EB) was also added together with the cocatalysts. A different preparation of supported catalyst was used which contained only 1.75% titanium.

TABLE IX

Run	Mmoles AlEt ₃ -	Mmoles Amide (2)	Mmoles Amine (2)	Mmoles EB	Rate	% HI
Control	0.4 (1)	0	0	0	963	49.0
Q	0.44	1.56	0.44	0.2	279	98.6

(1) 0.08 g. Catalyst

(2) B = Et₂Al-2,2,6,6-tetramethylpiperidide.

The results in Run Q show that very high stereospecificity (98.6% heptane insolubles) was obtained by the use of a dialkyl aluminum amide and two different Lewis bases

1 as modifiers for the trialkyl aluminum. The results are es-
2 pecially striking since the control run shows that the cata-
3 lyst gave very low stereospecificity (49% HI) in the ab-
4 sence of cocatalyst modifiers.

5. EXAMPLE XVII

6 The procedure of Example XIV, Run I, was followed
7 except that a diarylamide, diethyl aluminum di-ortho-tolylamide,
8 and a new preparation of the same type of supported catalyst
9 which contained 3.38% Ti were used. The polymerization rate
10 was 309 g/g. catalyst/hr. and the % HI = 93.4. Comparison with
11 Example XIV control and Run I shows that the diarylamide was
12 more effective than the diisopropylamide in increasing
13 stereospecificity.

14 Since many modifications and variations of this
15 invention may be made without departing from the spirit or
16 scope of the invention thereof, it is not intended to limit
17 the spirit or scope thereof to the specific examples thereof.

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CLAIMS:

1. A catalyst composition which comprises a mixture of:
 - (a) at least one supported Group IVA to VIII transition metal halide;
 - (b) a trialkyl metal cocatalyst, said trialkyl metal cocatalyst having the structure R'_3Y wherein R' is a C_1 to C_{20} primary alkyl, secondary alkyl, tertiary alkyl, neopentyl alkyl, branched alkyl, naphthenic or aralkyl group and Y is aluminium, gallium or indium;
 - (c) a nitrogen-containing metal alkyl compound having the structure R'_2YNR_2 or $R'XYNR_2$ wherein Y is Al, Ga or In, X is a halide and R' is a C_1 to C_{20} primary alkyl, secondary alkyl, tertiary alkyl, neopentyl alkyl, branched alkyl, naphthenic or aralkyl group and R is C_3 to C_{20} bulky alkyl, cycloalkyl, aryl or substituted aryl groups, with the proviso that the two R groups can be taken with N to form a pyrrolidyl or piperidyl and the alkyl substituted derivatives of pyrrolidyl and piperidyl, the mole ratio of said compound to said transition metal compound being from 0.5:1 to 200:1, and
 - (d) at least one Lewis base.
2. A composition according to claim 1 wherein Y is aluminum.
3. A composition according to either of claims 1 and 2 wherein said trialkyl metal cocatalyst is a trialkyl aluminium cocatalyst at a molar ratio of 1 to 50 to 50 to 1 based on said nitrogen containing metal alkyl compound.
4. A composition according to any one of the preceding claims wherein said nitrogen containing metal alkyl compound is diethylaluminium diisopropylamide, diethylaluminium dicyclohexylamide, diethylaluminium 2,2,6,6-tetramethylpiperidide or diethyl aluminium diorthotolyl amide.
5. A composition according to any one of the preceding claims wherein said transition metal compound is $TiCl_3$ on a support or $TiCl_4$ on a support.

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6. A composition according to any one of the preceding claims wherein said support is MgCl_2 .
7. A composition according to any one of the preceding claims wherein said Lewis base is an amine, ester, phosphine, ether, amide, sulfoxide, phosphine oxide, phosphate, phosphite, epoxide, saturated or unsaturated heterocycle, piperidine, pyrrolidine, ketone, tetrahydrofuran, secondary or tertiary aliphatic or aromatic amine.
8. A composition according to claim 7 wherein said Lewis base is ethyl benzoate.
9. A composition according to any one of claims 1 to 6 wherein said Lewis base is hindered.
10. A composition according to any one of the preceding claims wherein said R groups are aryl.



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EUROPEAN SEARCH REPORT

Application number
0015763
EP 80 30 0705

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<u>FR - A - 2 380 305</u> (EXXON) * Claims 1-5,7,8,10-13; page 4, lines 24-37; example 6; example 10, run AA; page 15, lines 14-17 *	1-8	
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	<u>FR - A - 1 294 416</u> (EASTMAN KODAK) * Abstract 1,a-f,2a,b *	1,4,10	
	--		
A	<u>FR - A - 1 123 617</u> (K. ZIEGLER) * Abstract 1; page 2, column 2, line 37 and following; page 3, lines 4-7; page 6, example 12 *	1,4,10	
	--		
	<u>US - A - 3 642 746</u> (N. KASHIWA et al.) * Claims 1-11; column 7, lines 29-40 *	1-3,5-8	

			TECHNICAL FIELDS SEARCHED (Int.Cl. ³)
			C 08 F 10/00- 4/60 4/02
			C 08 F 10/00- 10/14 110/00- 110/14 210/00- 210/18 4/60 4/02
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family. corresponding document
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
The Hague	11-06-1980	WEBER	